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(54) Title: USE OF MODIFIED POLYESTERS FOR THE WASHING OF COTTON-CONTAINING FABRICS (57) Abstract The present invention relates to the use of selected modified polyesters known for their soil-release properties as cleaning agents for cotton-containing fabrics, thus being able to provide a cleaning effect on such fabrics after only one laundering cycle, as compared to several cycles when functioning in the soil-release agent mode. The present invention also encompasses detergent compositions containing said modified polyesters and a cellulase enzyme, or a co-dispersing agent and/or a soil-antiredeposition agent.		

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**USE OF MODIFIED POLYESTERS FOR THE WASHING OF COTTON-
CONTAINING FABRICS**

Technical Field

The present invention relates to the use of modified polymers known for their soil-release properties, as cleaning agents for cotton-containing fabrics; the invention further relates to certain detergent compositions containing said modified polymers.

Background of the invention

Products used in laundering operation contain a number of ingredients which provide certain basic benefits. For example, laundry cleaning products are formulated with detergent surfactant systems to remove a variety of soils from clothes during washing. These laundry products can also include ingredients which provide through-the-wash fabric conditioning benefits such as softening and anti-static performance.

In addition to standard cleaning, softening and anti-static benefits, laundry detergent can also impart other desirable properties. One is the ability to confer soil release properties to fabrics woven from polyester fibers. The hydrophobic character of polyester fabrics makes their

laundering difficult, particularly as regards oily soil and oily stains. The oily soil or stain preferentially "wets" the fabric. As a result, the oily soil or stain is difficult to remove in an aqueous laundering process.

Certain polyesters have been found to be particularly useful as soil release compounds in laundry detergent composition. During the laundering operation, these soil release polyesters adsorb onto the surface of fabrics immersed in the wash solution. The adsorbed polyesters then form a hydrophilic film which remains on the fabric after it is removed from the wash solution and dried. This film can be renewed by subsequent washing of the fabric with a detergent composition containing the soil release polyesters.

Such polyesters are disclosed in e.g. US Patent 4 116 885 and 4 711 730.

Continuous effort has been put against improving soil release polyesters; in e.g. EPA 272 033 have been described such improved polyesters. More recently, EPA 311 372 has described further improved soil release agents consisting of sulfoaroyl end-capped polyesters.

It has now been surprisingly found that certain modified polyesters described in EPA 311 342 not only act as a soil release agents on polyester fabrics, but are also able to remove soils from cotton-containing fabrics and to disperse such soils, during the main laundering cycle of a laundry process.

It has further been found that the use of the modified polyesters herein in combination with cellulase enzymes as well as certain soil anti redeposition agents or co-dispersing agents or in combination with a selected class of nonionic surfactants provides unexpectedly improved cleaning benefits on cotton-containing fabrics.

Detailed Description of the Invention

The present invention is based on the discovery that the selected modified polyesters herein can act in a "surfactant" mode versus cotton-containing fabrics, thus being able to provide a cleaning effect on such fabrics after only one laundering cycle, as compared to several cycles when functioning in the soil-release agent mode.

The modified polyesters

The modified polyesters herein are random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target being to obtain is a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoid acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

Furthermore, it has been found that the combined use of the present modified polyesters with a cellulase enzyme and/or certain co-dispersing agents and/or certain nonionic surfactants provides superior cleaning benefits.

The Cellulase

The cellulase usable in the combination with the modified polyesters herein may be any bacterial or fungal cellulase, having a pH optimum of between 5 and 9.5.

Suitable cellulases are disclosed in GB-A-2 075 028; GB-A-2 095 275 and DE-OS-24 47 832.

Examples of such cellulases are cellulase produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly by the *Humicola* strain DSM 1800, and cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula Solander*).

The cellulase added to the composition of the invention may be in the form of a non-dusting granulate, e.g. "marumes" or "prills", or in the form of a liquid in which the cellulase is provided as a cellulase concentrate suspended in e.g. a nonionic surfactant or dissolved in an aqueous medium.

Preferred cellulases for use herein are characterized in that said cellulase they provide at least 10% removal of immobilized radioactive labelled carboxymethyl-cellulose according to the C14CMC-method described in EPA 350 098 at $25 \times 10^{-6}\%$ by weight of cellulase protein in the laundry test solution.

Most preferred cellulases are those as described in International Patent Application WO 91/17243. For example, a cellulase preparation useful in the compositions of the invention can consist essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from *Humicola insolens*, DSM 1800, or which is homologous to said 43kD endoglucanase.

The modified polyesters herein typically achieve their cleaning benefits on cotton-containing fabrics by being incorporated into a detergent composition including other deterative ingredients, at a level of from 0.025% to 10% by weight of the composition.

Alternatively, the modified polyester herein can be added separately, to the laundry cycle, in the form of a detergent additive: said additive possibly containing other selected detergent active materials, such as soil anti-redeposition agents and co-dispersing agents, and/or cellulase enzyme; in particular, the modified polyesters herein can be used to pre-treat cotton-containing fabrics, before the main wash cycle of a laundering process.

DETERGENT COMPOSITION

The detergent compositions herein can be in a liquid or granular form and are preferably delivered directly to the drum and not indirectly and via the outer casing of the machine. This can most easily be achieved by incorporation of the composition in a bag or container from which it can be released at the start of the wash cycle in response to agitation, a rise in temperature or immersion in the wash water in the drum. Such a container will be placed in the drum, together with the fabrics to be washed. Alternatively the washing machine itself may be adapted to permit direct addition of the composition to the drum e.g. by a dispensing arrangement in the access door.

When the compositions are in liquid form, a rigid container such as disclosed in EPA 151 549 can be used the detergent composition herein are preferably in granular form, and the container will be flexible, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in EPA no. 0 018 678. Alternatively it may be formed of a water insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as

disclosed in EPAs nos. 0 011 500, 0 011 501, 0 011 502, and 0 011 968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

In a variant of the bag or container product form, laminated sheet products can be employed in which a central flexible layer is impregnated and/or coated with a composition and then one or more outer layers are applied to produce a fabric-like aesthetic effect. The layers may be sealed together so as to remain attached during use or may separate on contact with water to facilitate the release of the coated or impregnated material.

An alternative laminate form comprises one layer embossed or deformed to provide a series of pouch-like containers into each of which the detergent components are deposited in measured amounts, with a second layer overlying the first layer and sealed thereto in those areas between the pouch-like containers where the two layers are in contact. The components may be deposited in particulate, paste or molten form and the laminate layers should prevent egress of the contents of the pouch-like containers prior to their addition to water. The layers may separate or may remain attached together on contact with water, the only requirement being that the structure should permit rapid release of the contents of the pouch-like containers into solution. The number of pouch-like containers per unit area of substrata is a matter of choice but will normally vary between 500 and 25,000 per square meter.

Suitable materials which can be used for the flexible laminate layers in this aspect of the invention include, among others, sponges, paper and woven and non-woven fabrics.

However the preferred means of carrying out the washing process according to the present invention includes the use of a reusable dispensing device having walls that are permeable to liquid but impermeable to the solid composition.

Devices of this kind are disclosed in EPAs Nos. 0 343 069 and 0 344 070. The latter Application discloses a device comprising a flexible sheet in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing cycle. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

The detergent compositions herein contain a surfactant.

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3 664 961 issued to Norris on May 23, 1972.

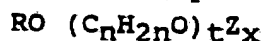
Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulfate surfactants in a weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C₁₂-C₁₈ fatty source preferably from a C₁₆-C₁₈ fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulfate surfactants are alkyl sulfates having from 12 to 18 carbon atoms in the alkyl radical, optionally in admixture with ethoxy sulfates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. Examples of preferred alkyl sulfates herein are tallow alkyl sulfate, coconut alkyl sulfate, and C₁₄-15 alkyl sulfates. The

cation in each instance is again an alkali metal cation, preferably sodium.

One class of nonionic surfactants particularly useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 5 to 17, preferably from 6 to 14, more preferably from 7 to 12. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

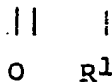
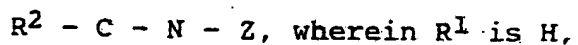
Especially preferred nonionic surfactants of this type are the C₉-C₁₅ primary alcohol ethoxylates containing 3-9 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol, the C₁₂-C₁₅ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol, and mixtures thereof.

Another suitable class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-3 0 070 077, 0 075 996 and 0 094 113.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C_8-C_{20} , preferably $C_{10}-C_{14}$ N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Another class of surfactants are amphoteric surfactants, such as polyamine-based species.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_8-C_{16} , preferably $C_{10}-C_{14}$ N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Mixtures of surfactant types are preferred, more especially anionic-nonionic and also anionic-nonionic-cationic mixtures. Particularly preferred mixtures are described in British Patent No. 2 040 987 and European Published Application No. 0 087 914. The detergent compositions can comprise from 1%-70% by weight of surfactant, but usually the surfactant is present in the compositions herein an amount of from 1% to 30%, more preferably from 10-25% by weight.

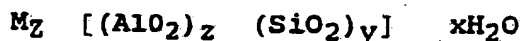
The detergent compositions herein also contain a builder

Builder materials will typically be present at from 5% to 80% of the detergent compositions herein. The compositions herein

are free or substantially free of phosphate-containing builders (substantially free being herein defined to constitute less than 1% of the total detergent builder system), and the builder system herein consists of water-soluble builders, water-insoluble builders, or mixtures thereof.

Water insoluble builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated Zeolite A, X, B or HS.

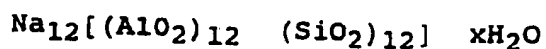
Preferred aluminosilicate ion-exchange materials have the unit cell formula



wherein M is a calcium-exchange cation, z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline containing from 10% to 28%, more preferably from 18% to 22% water.

The above aluminosilicate ion exchange materials are further characterized by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example microscopic determination utilizing a scanning electron microscope. The aluminosilicate ion exchange materials are further characterized by their calcium ion exchange capacity which is at least 200 mg equivalent of $CaCO_3$ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is described in detail in GB-1 429 143.

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available and can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US Patent No. 3 985 669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designation Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula



wherein x is from 20 to 30, especially 27. Zeolite X of formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 10.276\text{H}_2\text{O}$ is also suitable, as well as Zeolite HS of formula $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \cdot 7.5 \text{H}_2\text{O}$.

Another suitable water-insoluble, inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$). The high $\text{Ca}^{++}/\text{Mg}^{++}$ binding capacity is mainly a cation exchange mechanism. In hot water, the material becomes more soluble.

The water-soluble builder can be a monomeric or oligomeric carboxylate chelating agent.

Suitable carboxylates containing one carboxy group include lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831 368, 821 369 and 821 370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2 446 686, and 2 446 687 and U.S. Patent No. 3 935 257 and the sulfinyl carboxylates described in Belgian Patent No. 840623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates.

as well as succinate derivatives such as the carbomethyloxysuccinates described in British Patent 1 379 241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1 387 447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1 261 829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1 398 421 and 1 398 422 and in U.S. Patent No. 3 936 448, and the sulfonated pyrolysed citrates described in British Patent No. 1 082 179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1 439 000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis, cis, cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran-tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1 425 343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the preferred granular detergent compositions herein include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a water-soluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for the purposes of the invention include inorganic

materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

In a preferred embodiment of the present invention, the detergent compositions herein will contain a cellulase enzyme such as described above, at levels of from 0.025% to 10% of the composition.

In another preferred embodiment of the present invention, the detergent compositions or detergent additives herein will contain a soil anti redeposition or soil suspension agent, in combination with the modified polyesters herein.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, homo- or copolymeric polycarboxylic acids or their salts and polyaminoacid compounds. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers disclosed in detail in EPA 137 669, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. Polyaminoacid compounds such as those derived from aspartic acid are for instance disclosed in British patent application No. 9226942.2.

These materials are normally used at levels of from 0.025% to 5% by weight, of the compositions herein.

The present detergent compositions are preferably in granular form and more preferably in a "compact" form, i.e. having a density, which is higher than the density of conventional detergent compositions. The preferred density of the compositions herein ranges from 550 to 950g/liter, preferably 650 to 850g/liter of composition, measured at 20°C.

The present "compact" form of the most preferred compositions herein is best reflected, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form, in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition.

In the most preferred compositions herein, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

Inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulfates and chlorides.

A preferred filler salt is sodium sulfate.

The present compositions will typically include optional ingredients that normally form part of detergent compositions. Enzymes, optical brighteners, bleaches, bleach activators, suds suppressors, anticaking agents, dyes and pigments are examples of such optional ingredients and can be added in varying amounts as desired.

Enzymes such as proteases, lipases, or amylases are particularly desirable ingredients of the compositions herein.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4¹-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2¹ disulphonate, disodium 4, - 4¹-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2¹ - disulphonate, disodium 4,4¹ - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2¹ - disulphonate, monosodium 4¹,4¹¹ -bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4¹ -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2¹ - disulphonate, disodium 4,4¹ -bis-(4-phenyl-2,1,3-triazol-

2-yl)-stilbene-2,2¹ disulphonate, disodium 4,4¹bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2¹disulphonate and sodium 2(stilbyl-4¹¹-(naphtho-1¹,2¹:4,5)-1,2,3 - triazole-2¹¹-sulphonate.

Any particulate inorganic perhydrate bleach can be used, in an amount of from 3% to 40% by weight, more preferably from 8% to 25% by weight and most preferably from 12% to 20% by weight of the compositions. Preferred examples of such bleaches are sodium perborate monohydrate and tetrahydrate, percarbonate, and mixtures thereof.

Another preferred separately mixed ingredient is a peroxy carboxylic acid bleach precursor, commonly referred to as a bleach activator, which is preferably added in a prilled or agglomerated form in granular detergents. Examples of suitable compounds of this type are disclosed in British Patent Nos. 1586769 and 2143231 and a method for their formation into a prilled form is described in European Published Patent Application No. 0 062 523. Preferred examples of such compounds are tetracetyl ethylene diamine and sodium 3, 5, 5 trimethyl hexanoyloxybenzene sulphonate.

Bleach activators are normally employed at levels of from 0.5% to 10% by weight, more frequently from 1% to 8% and preferably from 2% to 6% by weight of the composition.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m²/g intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200 000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight. The incorporation of the suds modifiers is preferably made as separate particulates, and this permits the inclusion therein of other suds controlling materials such as C20-C24 fatty acids, microcrystalline waxes and high MW copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al U.S. Patent No. 3 933 672.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898.

Organic fabric softening agents include the water-soluble tertiary amines as disclosed in GB-A-1 400 898. Organic fabric softening agents include the water-insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-O 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-O 026 527 and EP-B-O 026 528 and di-long-chain amides as disclosed in EP-B-O 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-O 299 575 and 0 313 146.

In the preferred granular detergent compositions herein, levels of smectite clay are normally in the range from 5% to 20%, more preferably from 8% to 15% by weight with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or di-long-chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water-soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

The compositions herein may also contain dye-transfer inhibiting agents such as polyvinylpyrrolidones having a molecular weight from 5 000 to 2 200, typically present in the preferred granular detergent compositions herein, at level such as to deliver from 5 to 500 mg/l of said polyvinyl pyrrolidones in the wash solution.

EXAMPLES

The following examples illustrate the invention and facilitate its understanding.

The abbreviations for the individual ingredients have the following meaning:

- LAS: sodium salt of linear dodecyl benzene sulfonate
AS: sodium salt or C14-15 alkyl sulfate
TAS: sodium salt of tallow alcohol sulfate
FA45E7: fatty alcohol (C14-C15) ethoxylated with about 7 moles of ethylene oxide
FA25E3: fatty alcohol (C12-15) ethoxylated with about 3 moles of ethylene oxide
CAT: C12 alkyl trimethyl ammonium chloride
Clay: smectite clay
Zeolite A4: sodium salt of zeolite 4A with average particle size between 1 - 10 micrometer
SKS-6: crystalline layered silicate (Hoechst)
Copolymer AA/MA: copolymer of acrylic acid and maleic acid
PAA: Polyacrylate polymer
CMC: carboxymethylcellulose
Phosphonate: sodium salt of ethylenediamine tetramethylene phosphonic acid
EDTA: sodium salt of ethylenediamine tetra acetate
PB1: $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
TAED: tetra acetyl ethylene diamine
PVP: Polyvinylpyrrolidone
Silicate (R=n): $\text{SiO}_2/\text{Na}_2\text{O}=\text{n}$
Cellulase: 43kD species according to the description herein above
Amylase: Termamyl 60T (Novo-Nordisk)
Lipase: Lipolase 100T (Novo-Nordisk)
Protease: Savinase 4T (Novo-Nordisk)
SSS: Suds Suppressing System (silica/silicone mixture)

The modified polyester used throughout the following examples correspond to the species described in claim 2 herein.

The method of preparation was as follow:

The process of preparation of the selected polyester herein includes mixing all the monomers in a round bottomed flask, stirring at 180°C, until a clear solution results, and continue stirring for 24 hours. Then transferring the contents of the

round bottomed flask to a further single necked round bottomed flask (typically 1 litre), heating under vacuum for 45 minutes at 200°C, removing from flask and cooling. A clear glass solid is obtained, which is then crushed gently to be used.

Example 1:

The following detergent composition was prepared.

	<u>.% by weight</u>
LAS	9
TAS	3
FA45E7	2.5
ZEOLITE	33
SODIUM CITRATE	21
SODIUM CARBONATE	3
SODIUM SULPHATE	5
PAA	3.5
PROTEASE	1.6
CELLULASE	0.5
MODIFIED POLYESTER	0.5

Testing procedure:

A bundle of soiled fabrics containing fabrics which were stained with a range of stains such as particulate soils, greasy soils, enzymatic soils and bleachable soils on cotton and polycotton fabrics were washed in a compact detergent with the formulation as shown. One half of each bundle was washed with detergent composition as shown and the other half was washed with the same composition without the cellulase. The testing was carried out at 40°C in water of 25°H (German hardness). All testing was repeated 4 times.

Stain removal was evaluated relative to a reference stain of each type previously washed under identical conditions. The formulation used for the washing of the reference fabrics contained no modified polyester or cellulase.

Stain removal was evaluated using the well known schefe scale of panel score units determined by two judges as follows:

- 1 = I think there is a difference between the two stains.
- 2 = There is certainly a difference between the two stains.
- 3 = There is a big difference between the two stains.
- 4 = There is a black and white difference between the two stains.

The average data compared to the reference fabric was calculated. The results on the greasy stains on polycotton material were as follows.

<u>Stain</u>	<u>Preference for example 1</u> <u>composition</u> <u>versus reference</u>
Dirty motor oil	+1.1*
Make up	+0.5*

* Statistically significant

Example 2:

A detergent of formulation similar to that described in example 1 was used to wash a bundle of soiled fabrics which were stained with a range of soils of particulate, greasy, enzymatic and bleachable types. One half of each bundle was washed in the formulation described in example 1, the other half of the bundle was washed in the identical formula without modified polyester. The conditions used for washing these bundles were 40°C and 25 H

water. 4 replicates of each test were carried out and the samples were graded accordingly to the % stain removal. This was calculated using the McBeth (colour spectrometer) using the conventional 1 a b system. The tests were repeated using different levels of modified polyesters between 0.025% and 10% by weight of the detergent composition.

The results are detailed below:

Level	0.025%	0.1%	0.5%	10%
Stain removal average greasy on polycotton	52%	64%	69%	73%

Typical greasy stains considered include dirty motor oil, shoe polish and make up.

Figures quoted are average %stain removal enhancement above the reference product.

Example 3:

Enhanced greasy stain removal by the combination of modified polyester and carboxy methyl cellulose.

Polycotton swatches were pretreated a number of times with a deterative formulation containing the carboxy methyl cellulose (CMC). The purpose of this was to give the fabric a history of CMC deposition onto the cotton of the polycotton. The polycotton was then dried and stained with dirty motor oil (DMO). One half of the stains was washed in a deterative formulation similar to that described in example one to act as a reference whilst the other half was washed in the same formulation only containing the modified polyester herein.

The swatches were graded by calculating the % stain removal from each tracer using the hunter colour lab system. All data was also compared to swatches which had been treated in exactly the same way as described above only with a deterative formulation containing soil release polymer and no CMC. The results are described below.

	<u>Reference</u> <u>(CMC only)</u>	<u>Modified</u> <u>polyester</u> <u>only</u>	<u>CMC/modified</u> <u>polyester</u>
Average % stain removal	21%	43%	79%

Test conditions 40°C/25°H water - 4 replicates

Example 4:

Pretreatment solution compositions containing the modified polyester herein were prepared as shown below

<u>Formulation:</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Modified polyester	0.5	1.0	3.0	5.0	6.0	6.0
LAS	40	50	75	75	-	-
FA45E7	13	17	17	-	30	22
Maleic/acrylic copolymer	46.5	32	5.0	20	64	72

All the solutions were used to pretreat polycotton fabrics prior to washing which had previously been stained with a range of greasy type stains such as dirty motor oil, sun tan lotion make up and lipstick.

All fabrics which had previously been treated with any of the compositions described showed marked improvement in the stain removal from the polycotton when compared to an untreated stain.

The following compact detergent compositions were also prepared:

COMPACT DETERGENT COMPOSITIONS
(all levels in % by weight)

[illegible]

CLAIMS:

1. A detergent composition or additive comprising a surface-active agent, a builder, and from 0.025 to 10% of a modified polyester, the polyester being a random copolymer of dimethyl terephthalate, dimethyl sulfoisophthalate ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulfobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol.
2. A detergent composition or additive according to Claim 1 wherein said polyester comprises about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol, about 13% by weight of sulfo benzoid acid and about 15% by weight of sulfoisophthalic acid, and has a molecular weight of between 2,500 and 3,500.
3. A granular detergent composition or additive according to Claim 1 or 2 comprising no more than 15% by weight of inorganic filter salt and having a density of 550 to 950 g/liter of composition.
4. A detergent composition or additive according to Claim 1 which in addition comprises a soil antiredeposition or soil suspension agent selected from the group of carboxymethylcellulose polycarboxylates, polypeptide compounds, and mixtures thereof.
5. A detergent composition or additive according to Claim 1, 2, 3 or 4 further comprising a cellulase enzyme.
6. The use of a modified polyester, said polyester being a random copolymer of dimethyl terephthalate, dimethyl sulfoisophthalate ethylene glycol and 1-2 propane diol, the end groups consisting primarily of

sulfobenzate and secondarily of mono esters of ethylene glycol and/or propane-diol, as a cleaning agent for cotton-containing fabrics, said fabrics being contacted with an aqueous laundry liquor containing said compounds and subjected to one laundering cycle.

7. The use of Claim 6 wherein said polyester contains about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol, about 13% by weight of sulfo benzoid acid and about 15% by weight of sulfoisophtalic acid, and has a molecular weight between 2,500 and 3,500.
8. The use of Claim 6 or 7 wherein said polyester is combined with a cellulase enzyme.
9. The use of any one of Claims 6-8 wherein said polyester is incorporated into a detergent composition including other deterative ingredients, at a level of compound of from 0.025% to 10% by weight of the composition.
10. The use of any one of claims 6-8 wherein said polyester is incorporated in a detergent additive composition for the pre-laundering of cotton-containing fabrics.
11. The use of Claim 9 or 10 wherein said detergent composition or additive composition is put in a container able to release the composition at the start of the laundering cycle or of the pre-laundering cycle, and said container is placed in the drum of a washing machine, together with the fabrics to be laundered and/or pre-laundered.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/03245

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :IPC (5): C11D 3/22, 3/32, 3/34, 3/37, 3/386; DO6M 13/256

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/8.7, 174.12, 174.18, 174.23, 546, DIG.15

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>X</u> Y	US, A, 4,976,879 (Maldonado et al.) 11 December 1990, see col. 5, lines 41-67; col. 6, lines 42-50 and lines 62-64; col. 7, lines 19-28; col. 17, line 35- col. 19, line 29; Example X; col. 29, line 58- col. 30, line 60; Examples XVI-XVIII.	<u>1,2,3,6,7</u> 1-4, 6-8
Y	WO, 91/17243 (Novo Nordisk A/S) 14 November 1991, see abstract; p. 10, line 1- p. 11, line 24.	8
Y	US, A, 4,435,307 (Barbesgaard et al.) 06 March 1984, see col. 2, lines 20-46; col. 5, line 30- col. 6, line 17; Examples 2-5, Table 1.	8

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be part of particular relevance
* E	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* L	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* O		document referring to an oral disclosure, use, exhibition or other means
* P	* &	document published prior to the international filing date but later than the priority date claimed
		document member of the same patent family

Date of the actual completion of the international search

22 JUNE 1993

Date of mailing of the international search report

05 AUG 1993

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/03245

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB, A, 20952275 (Kao Soap Co., Ltd.) 29 September 1982, see p.2, lines 4-39; p. 2, line 54- p. 10, line 4; Examples 1-3, 5, 6.	4,8
Y	US, A, 4,116,885 (Derstadt et al.) 26 September 1978, see col. 3, line 52- col. 4, line 17; col. 10, lines 56-65.	4,8
A	US, A, 4,711,730 (Gosselink et al.) 08 December 1987, see entire document in general.	1-4, 6-8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03245

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5, 9, 10 & 11
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/03245

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

U.S. CL.: 252/8.7, 174.12, 174.18, 174.23, 546, DIG. 12, DIG. 15